Influence of CO_2 upon UV-Vis spectroscopy of silica-tetra-3,4-dimethoxy-phenyl-porphyrin hybrid nanomaterial

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Abstract
A symmetrical substituted aryl porphyrin was incorporated by sol-gel method to generate a silica hybrid nanomaterial that preserves the UV-vis absorption properties of bare porphyrin. The novel hybrid demonstrated to be a sensitive material for CO_2 detection. The sol-gel synthesis was monitored by UV-vis spectroscopy. Atomic force microscopy was performed for the hybrid before and after CO_2 detection and important changes in the aggregation behavior of the nanomaterial were observed.

Keywords: porphyrin-silica hybrid, sol-gel, UV-vis, CO_2 detection, AFM

Introduction
In 1997, for the first time a phosphorescence signal from a porphyrin encapsulated in a sol-gel matrix was used for gaseous oxygen sensing [1]. This result accelerated work into other optical sensors using water-insoluble luminescent dye/sol-gel matrices.
Sol-gel process affords easy immobilization of any porphyrin retaining the optical and sensing properties of the dye, due to the high homogeneity of the porphyrin molecules into the sol-gel matrices. The critical issues remain the tailoring of sol-gel materials to inhibit leaching of porphyrin, and to achieve enhanced sensor performance in terms of stability, response time, sensitivity, repeatability and selectivity.
Based on our previous studies regarding CO_2 detection [2] in this paper the porphyrin was incorporated into a silica matrix by sol-gel method in two steps acid-base catalysis and used as optical sensor for the detection of CO_2 in wet environment.

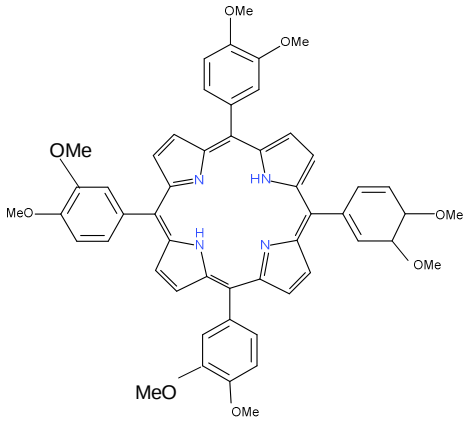

Figure1. Structure of tetra (3,4-dimethoxy-phenyl)-porphyrin.

Experimental

2.1. Reagents

All reagents used in this work were *p a* grade provided by Merck, Fluka and Sigma-Aldrich.

2.2. Sol-gel synthesis was done by adapting previously reported paper [3]. A mixture of H_2O (2,730g; 0,152mmol) and HCl 37% (0,037g; 1,01 mmol) were added by dripping under continuous stirring to a solution of TEOS (7,9g; 0,038moli) dissolved into EtOH (6,98g; 0,152 mmol) containing a mixture of 8 mg porphyrin ($0.88x10^{-5}$ mmol) dissolved in 14 ml THF. The molar ratios were: TEOS:EtOH:H_2O:HCl= 1:4:4:0,01. After 40 minutes, the second basic step was started by slowly adding of NH3 1.6g (solution of NH_3 25%+9g H_2O). Transparent gel colored in violet was obtained instantly.

2.3. Apparatus

UV-visible spectra were registered on JASCO UV- V-650 visible spectrometer using 1 cm pass cells. Atomic force microscopy (AFM) investigations were performed on Nanosurf®EasyScan 2 Advanced Research AFM. AFM images were obtained in contact mode.

Results and discussion

The hybrid material was characterized after first step of acid catalysis and in the final step of base catalysis. As revealed by Figure 2, the properties of porphyrin are preserved in both steps of catalysis. Our interest was to incorporate into the hybrid a porphyrin that is neutral, not a protonated one, so that we choose for the tests to CO_2 detection the hybrid preserving the properties of the initial porphyrin base that is the hybrid after gelation in the basic step.

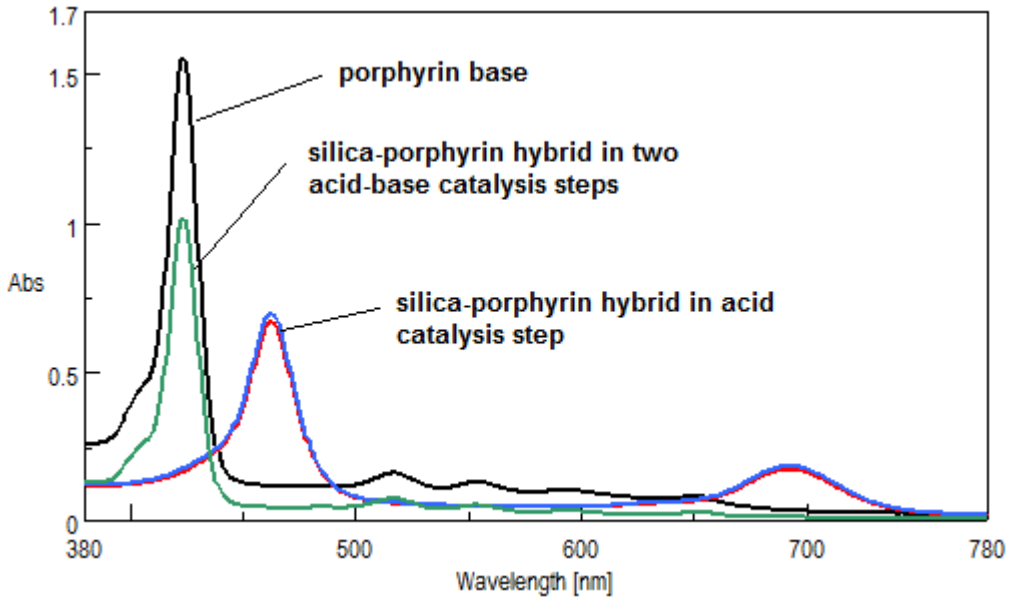

Figure 2. The UV-vis of the bare porphyrin and of the hybrids, at the same concentration in THF

The selected hybrid was further subjected to test to CO_2 and by increasing the quantity of gas introduced in the vial containing the gel (rate of 1µL/min), the intensity of the Soret band of the nanomaterial increased also, as presented in Figure 3. The dependence between the intensity of the Soret band of the silica-porphyrin hybrid and the CO_2 concentration is linear. A very good correlation coefficient is obtained.

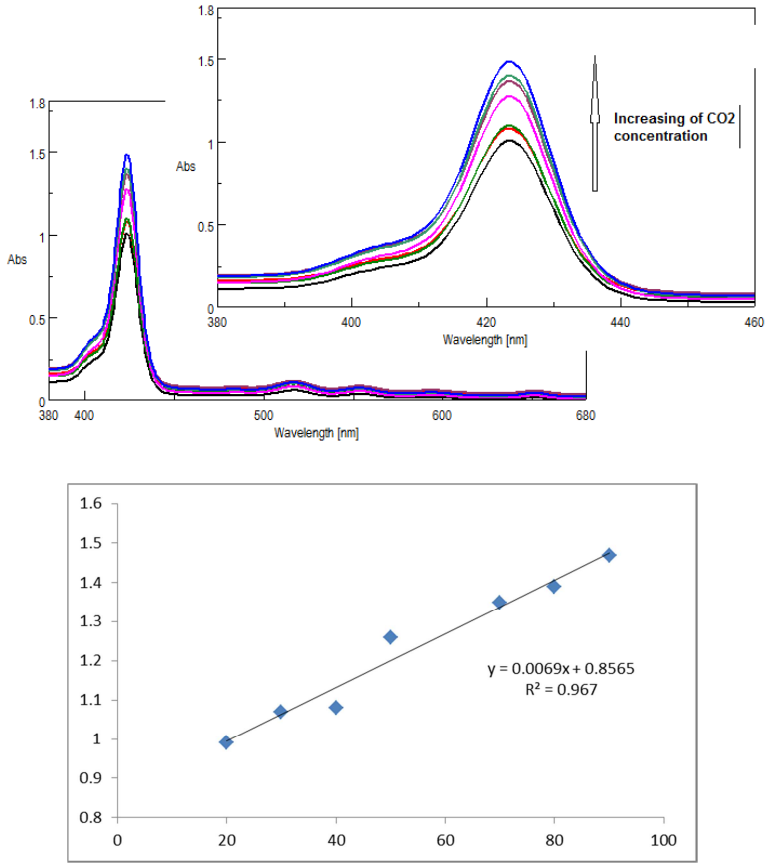

Figure 3. UV-vis spectra showing the linear dependence between CO_2 increasing of concentration and the increase of Soret band intensity for porphyrin-silica hybrid.

Due to the fact that the shape of the spectrum does not change during experiments we cannot presume that the mechanism of detection is based on the increase of acidity of the medium by CO_2 introduction. So other hypothesis can be some adsorption phenomena of CO_2 that might be accompanied by morphology and topography changes of the hybrid material. The aggregates of hybrid before CO_2 addition, investigated by AFM, look uniform, with small pores and with mean surface of islands of 0.0025 μm^2 as presented in Figure 4.

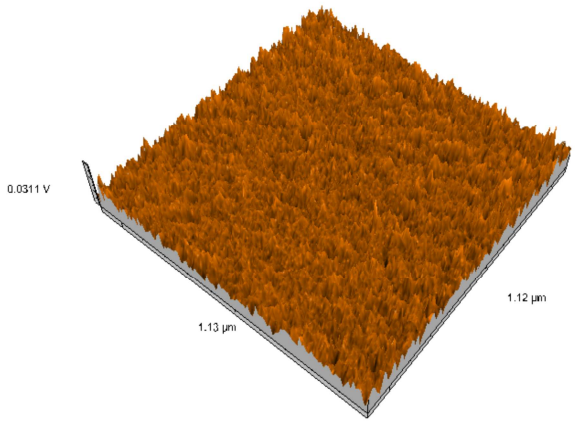

Figure 4. The surface image of hybrid nanomaterial before CO_2 addition.

The aggregates of hybrid after CO_2 interference are significantly bigger, look like irregular straw –type assemblies having the height of 68 nm, the mean surface of 0.0181 μm^2 and the

mean volume of 0.00013 µm^3. The diameter is varying in the range of 366 nm up to 791 nm (Figure 5).

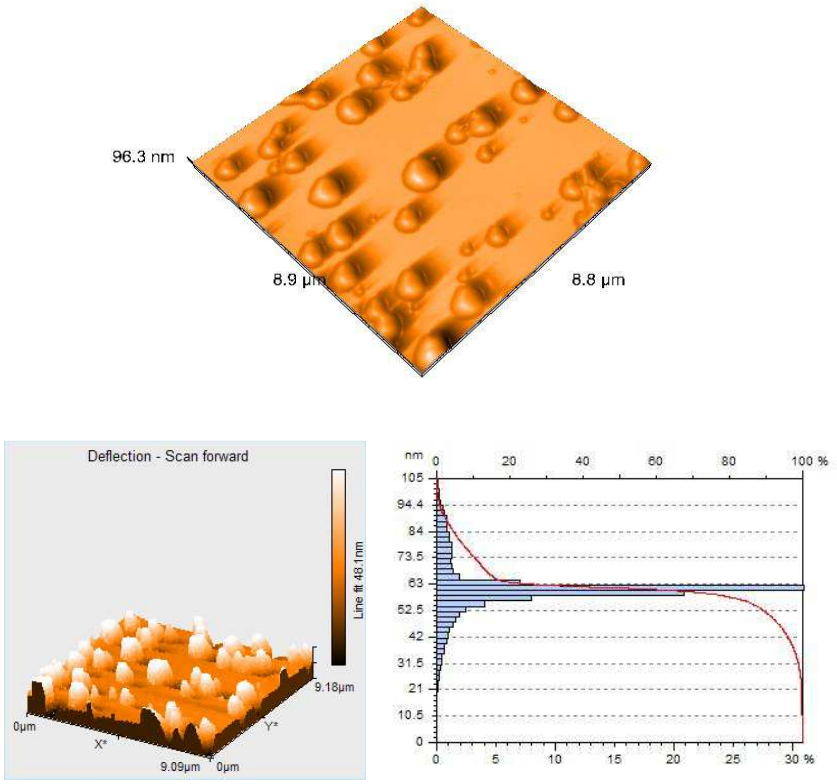

Figure 5. The surface image of hybrid nanomaterial after CO_2 addition.

Conclusion

A symmetrical A_4B substituted porphyrin was incorporated into a silica matrix by sol-gel method in two steps acid-base catalysis and used as optical sensor for the detection of CO_2 in wet environment.

By increasing the quantity of CO_2 gas introduced in the vial containing the gel the intensity of the Soret band of the nanomaterial increased also, the dependence between being linear.

AFM studies show important changes regarding the surface morphology before and after CO_2 addition to the hybrid nanomaterial, these indicating a probable absorption mechanism, not one based on acidity changes, as expected.

Acknowledgements

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References

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